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SCIENTIFIC PAPER

UDC 677:677.11:66

THE STUDY OF DIRECT DYE SORPTION ON FLAX FIBERS DURING DYEING

Article Highlights

- Dyeing of a linen fabric with direct dye gives good results with a high degree of exhaustion
- Increasing the dye concentration during dyeing decreases the degree of exhaustion
- Longer dyeing time gives a greater degree of dye exhaustion
- Larger amount of dye or a longer dyeing period yields a greater amount of adsorbed dye
- The Flory-Huggins model is preferred to describe the direct dye adsorption on flax fibers

Abstract

This article presents the study of direct dye sorption onto the flax fiber during the dyeing process in the presence of an inorganic electrolyte. The previously prepared linen fabric was subjected to dyeing by a standard process, varying in concentration and time of dyeing. The results are satisfactory considering that they reveal the character of the direct dye sorption for fibers, as well as the capacity and energy adsorption, on the basis of which the process of dyeing can be optimized. The increase of dye concentration in the solution during dyeing decreases, and longer time of dyeing increases the degree of exhaustion. The adsorbed amount of adsorbate on the adsorbent rises during the increase of initial concentration and dyeing time. Langmuir, Freundlich, Temkin and Flory-Huggins models can be used to describe adsorption of a direct dye onto the linen fiber, having in mind the advantage of Flory-Huggins model because of its characteristics in the description of the sorption and maximum values of the coefficient of determination as well.

Keywords: dyeing, flax, Freundlich, Flory-Huggins, Langmuir, Temkin.

Due to their very good mechanical properties, thermostability, raw material reproducibility and biodegradability, natural fibers remain up-to-date for use in textiles where they can substitute artificial materials equally. Lately, because of the clear human tendency for natural materials and renewable resources, the interest for products from flax has increased, firstly in clothing and home textiles, and products for technical purposes (automotive industry, paper industry, protective textiles, building industry, composites, etc.). This presumes continuous improvement of the pre-dyeing preparation process and the dyeing process itself, as the final stage prior to final commercial pro-

duct. Of course, if necessary, final special finishing procedures may also be included to achieve special effects on textiles for clothing or technical use [1].

Flax fibers have similar mechanical properties like some artificial fibers, but due to their micro-morphological characteristics, they are less dense, with rough surface, specific layered structure, air-permeable and absorptive properties. Flax fibers as textiles made from them have weaker resistance to warping, good moisture absorption and, in accordance with these, weaker resistance to microorganisms, and with composite material, problems due to insufficient adhesiveness with the matrix are present. Flax is a very demanding substrate for preparation and dyeing processes due to its chemical composition and morphology. When compared to cotton, flax is poorer in pulp and richer in impurities [2].

It is well-known that linen textile materials are relatively more difficult to dye, due to the presence of large quantities of lignin and hemicellulose, as well as

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Paper received: 3 May, 2020

Paper revised: 2 November, 2020

Paper accepted: 9 November, 2020

<https://doi.org/10.2298/CICEQ200503043V>

their relatively greater crystallinity of the fibers that makes difficult the migration of dye molecule into the fiber. In order to solve this problem, special methods of preparation and dyeing itself are used, while studying the mechanism of binding and dye sorption, in order to identify and find the most suitable conditions for dyeing [3].

The dyeing of flax or similar cellulosic natural materials is usually done by direct or reactive dyes. Direct dyes have almost the lowest stability in comparison with all other known dyes, resulting in uneven dyeing with the present dye differences or differences in dyeing stability [3]. Despite the seemingly unstoppable rise in popularity of reactive dyes in recent decades and the fact that direct dyes represent only about 10-12% of dyes for cellulose fibers, the number of direct dyes used in dyeing is, however, significant. The reasons for the commercial acceptance of direct dyes include the inherent simplicity of the dyeing process, as well as the ability of dyes to typically give light shades, and moderate-to-good light durability and are low-cost [4].

In all dyeing processes of cellulose fibers with direct dye by the process of exhaustion, the main ingredient is an inorganic electrolyte. The use of inorganic electrolytes has attracted significant research interest, and many theories have been proposed in order to explain its impact on the dye exhaustion. However, none of these theories describe exactly the role of the inorganic electrolyte in direct color exhaustion. Also, no interpretation, derived from the proposed theories, can now be absolutely accepted as a physicochemical mechanism by which direct dye is adsorbed for cellulose fibers [5].

In order to contribute to dyeing of flax with direct dyes, this article has studied the character and mechanism of dye sorption by modeling the flax dyeing process for the additional knowledge of the nature of the interaction, diffusion, etc. based on which the process of dyeing can be optimized with the tendency of achieving the maximum effect and minimal costs.

EXPERIMENTAL

Materials and methods

Raw 100% linen fabric was used in the plain weave. The basic characteristics of the fabric are: warp and weft counts, 70 and 60 tex, respectively; area density, 240 g m⁻²; ends cm⁻¹ × picks cm⁻¹, 16 × 15.

C.I. Direct Red 81 was used for the dyeing process of linen fabric. Prior to dyeing, the fabric underwent scouring and bleaching processes according to standard procedures. The dyeing of thus prepared

linen fabric (1 g) was carried out in a bath of constant total volume of 0.1 dm³, at 90 °C in the presence of Glauber's salt (5 g dm⁻³) and a dye. Dye concentrations were 10, 20, 30, 40, 50 and 60 mg dm⁻³. The dyeing process took 5, 10, 20, 30, 40, 50 and 60 min. After completed dyeing, the fabric sample was removed from the bath and the rest of the solution was cooled and the absorbance was measured on a spectrophotometer (Cary 100 Conc UV-Vis, Varian). The absorption maximum of wavelength for the used direct red dye was 490 nm.

The degree of exhaustion (%) of the dye was calculated using the form [6]:

$$\text{Degree of exhaustion} = 100 \left(1 - \frac{A_1}{A_0} \right) \quad (1)$$

where: A_0 and A_1 - the absorbance of the original and dyeing residual solution, respectively.

The adsorption capacity, $q_{t,e}$ (amount of adsorbed dye per unit mass of linen fabric) was obtained in the following way [6]:

$$q_{t,e} = \frac{C_0 - C_{t,e}}{w} V \quad (2)$$

where: $q_{t,e}$ - the adsorption capacity at the time of dyeing t and in equilibrium, respectively, mg g⁻¹; C_0 - initial dye concentration, mg dm⁻³; $C_{t,e}$ - dye concentration in solution at the time of dyeing t and in equilibrium, respectively, mg dm⁻³; w - weight of the linen sample, g; V - volume of solution for dyeing, dm³.

For modeling of flax dyeing, various adsorption models were used: Langmuir, Freundlich, Temkin and Flory-Huggins.

The Langmuir adsorption isotherm describes adsorption on a homogeneous surface of adsorbents containing a limited number of identical adsorption sites and the absence of interaction between the adsorbed molecules.

The Langmuir adsorption model is presented as follows [7]:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0} \frac{1}{C_e} \quad (3)$$

where: q_e - the amount of adsorbate adsorbed per unit mass of adsorbent in equilibrium, mg g⁻¹; Q_0 - the adsorption capacity, mg g⁻¹; b - adsorption energy, dm³ mg⁻¹; C_e - equilibrium concentration of adsorbate-direct dye in solution, mg dm⁻³.

The Freundlich adsorption isotherm is empirical in nature and describes adsorption on an energetically heterogeneous surface on which molecules are adsorbed in interaction. This model describes well the multilayer adsorption.

Freundlich's model is shown as [7]:

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (4)$$

where: K_F ($\text{mg g}^{-1} (\text{dm}^3 \text{mg}^{-1})^{(1/n)}$) and n_F - constants characteristic of the predicted system: adsorbent, adsorbate and solvent.

Temkin isotherm is based on the following assumptions: the heat of adsorption of molecules on the surface of the adsorbent is linearly reduced with an increase in coverage degree and adsorption is characterized by a uniform distribution of the binding energy of the molecules at the surface of the adsorbent.

Temkin isotherm is shown by the following equation [7]:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (5)$$

where: q_e - the adsorption capacity in the equilibrium time mg g^{-1} ; C_e - equilibrium concentration of adsorbate in solution, mg dm^{-3} ; K_T , $\text{dm}^3 \text{mg}^{-1}$ and B_T - Temkin constants, the first of which represents adsorbate-adsorbent interactions and the second is related to the heat of adsorption b_T , J mol^{-1} :

$$B_T = \frac{RT}{b_T} \quad (6)$$

The Flory-Huggins model was used to determine the surface coverage characteristics of the adsorbent by adsorbate.

Linear form of Flory-Huggins equation looks like the following [8]:

$$\ln \frac{\theta}{C_0} = \ln K_{FH} + n_{FH} \ln(1-\theta) \quad (7)$$

where: $\theta = (1 - C_d/C_0)$ - degree of surface coverage; n - number of dye molecules that occupy the adsorption positions; K_{FH} - Flory-Huggins equilibrium constant, $\text{dm}^3 \cdot \text{mg}^{-1}$.

The K_{FH} and ΔG^0 are related as follows [8]:

$$\Delta G^0 = -RT \ln K_{FH} \quad (8)$$

where: ΔG^0 - the standard change of free energy, J mol^{-1} ; R - the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; T - temperature, K.

The Flory-Huggins isotherm is also important in adsorption studies because the degree of surface coverage is related to the sticking probability of adsorbate to the adsorbent by the equation [9]:

$$S^* = (1-\theta) \exp \frac{-E_a}{RT} \quad (9)$$

where: S^* - sticking probability; E_a - activation energy, J mol^{-1} ; R - the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; T - temperature, K.

Dyeing of linen fabrics has been performed by direct dye CI Direct Red 81, molecular formula $\text{C}_{29}\text{H}_{19}\text{N}_5\text{Na}_2\text{O}_8\text{S}_2$ and a molar mass of 675.6 g mol^{-1} , at $95 \text{ }^\circ\text{C}$. According to the molecular structure, this dye belongs to the double azo class and structural formula is shown in Figure 1 and it is used for dyeing of natural cellulose and chemical cellulosic fibers.

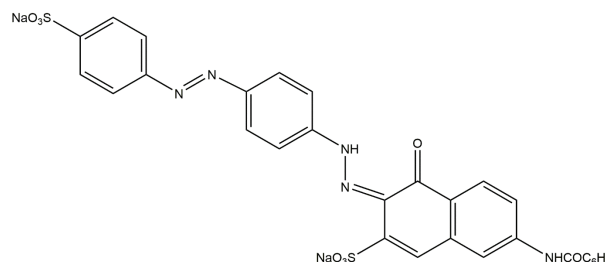


Figure 1. Structure of the applied direct dye C.I. Direct Red 81 (by software ChemBioDraw Ultra 14.0).

RESULTS AND DISCUSSION

In order to describe the processes at direct sorption of flax fiber in the presence of Glauber's salt, it is necessary to mention the following details. In a dyeing bath, flax fiber is negatively charged due to the ionization of cellulosic fibers, and the same applies to the dye (direct dye is anionic in aqueous solution). For effective sorption, it is necessary to reduce or remove the negative charge from the fibers, thereby improving their adsorption capacity for anionic direct dye bonding [10].

Generally, a dye is present in the bath in the form of molecules, micelles, aggregates and solids. When a dye is in the form of molecules and smaller micelles it can be adsorbed by cellulose fibers. Due to its inherent high solubility in electrolyte-free water, direct dye shows an innate tendency to remain in the aqueous phase (*i.e.*, in the bath) rather than switch to fibers. On the other hand, since the solubility of direct dye in water is significantly reduced in the presence of inorganic electrolytes, the predisposition of dye to favor the aqueous phase is significantly reduced, which is why it favors the transfer of dye onto the fiber when accelerating the absorption (exhaustion) of dye [11].

Nature of substantivity of direct dye-cellulose fiber is usually interpreted through various intermolecular interactions (*e.g.*, ion-ion interactions, hydrogen bonds, van der Waals interactions, etc.), which are also affected by the specific properties of the dye molecules and macromolecules of the fibers (*e.g.*, planarity, number and position of polar groups, sol-

ubilizing groups, orientation of aromatic centers, etc.) [12,13].

The influence of the initial dye concentration on its exhaustion and the amount of adsorbed dye for the fiber, over time, is shown in the diagram in Figure 2. As the initial dye concentration increases, the degree of exhaustion decreases depending on the dyeing time. Observing each exhaustion curve, at lower initial dye concentrations, in the beginning the decrease in the percentage of the degree of exhaustion is somewhat slower, and at the end, *i.e.*, at higher initial dye concentrations, this decrease in the percentage of the degree of exhaustion is somewhat steeper. This is especially true for exhaustion curves with a longer dyeing time, of 40-60 min.

As expected, the shortest dyeing time (5 min) causes the lowest degree of exhaustion, while the longest one (60 min) gives the highest value of this parameter.

In the diagram of the same figure, it is also noticeable that with the increase of the initial dye concentration, the adsorption capacity, q_t , increases sharply, continuously over time. This is especially true for curves for times of 20-60 min, while for the shortest time of 5 min, a curve is noticeable that almost horizontally follows the coordinate axis of the abscissa. As these curves approach the highest initial concentrations, the growth of q_t is somewhat milder, a slowdown occurs because the dye is adsorbed on the fiber surface and the rest of the dye molecules are evenly distributed in the dye bath due to the thermal

movement of the dye molecules. A diffusion adsorption layer is formed at the interface (contact surface). The dye concentration was gradually reduced in the diffusion adsorption layer, until it does not become similar to the concentration in the bath for the dyeing [14,15].

Figure 3 shows a diagram explaining the effect of contact time or length between adsorbate (dye) and adsorbent (flax fibers) on dye exhaustion during dyeing, for different initial concentrations of direct dye. In the beginning, at all initial concentrations, there is a sudden increase in dye exhaustion, so that after about 10 min of dyeing until the end of dyeing, this trend will be somewhat milder.

In Figure 4, the diagram shows the changes in the concentration of dye in solution and on flax fiber during dyeing for different initial concentrations. A relatively mild change in the dye concentration of dye bath is noticed with the growth of dyeing time, which is more intense in the beginning, and then becomes slower. The higher dye concentrations have a steeper fall curve in the beginning of dyeing in comparison with lower concentrations, which is connected to the rapid dye binding for the fibers in the beginning, regarding a large difference in the gradient of concentration. The beginning of dyeing results in faster dye binding onto the fiber, *i.e.*, higher amount of adsorbed dye per unit mass of adsorbent, and later with the duration of dyeing, this binding becomes slower. At the highest applied initial dye concentrations and the longest dyeing, the largest dye adsorption of the fiber occurs.

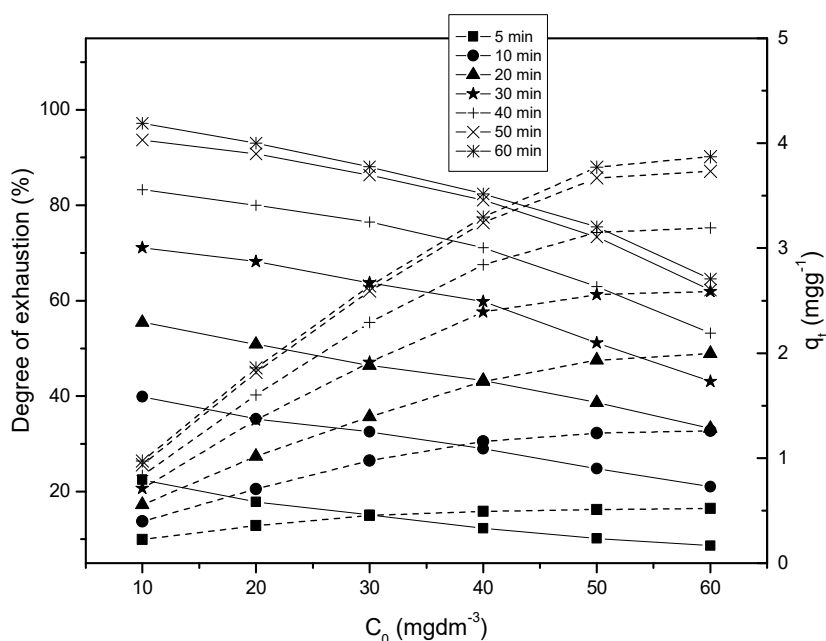


Figure 2. The effect of initial dye concentration on the degree of exhaustion (full line) and adsorption capacity (interrupted line) during dyeing.

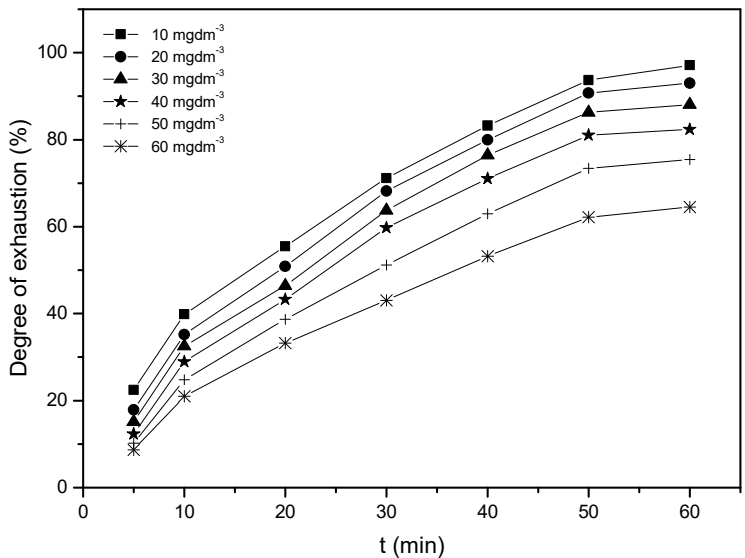


Figure 3. Influence of time on the degree of direct red dye exhaustion during linen dyeing.

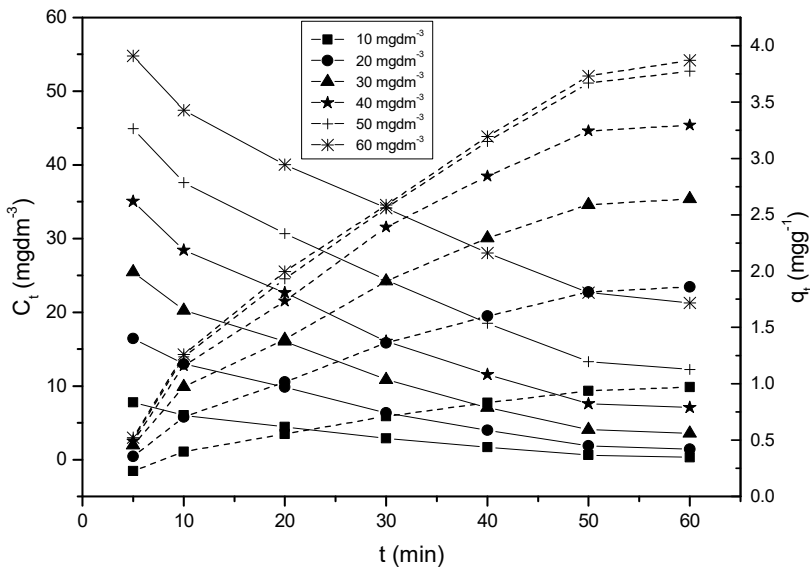


Figure 4. Change in concentration (full line) and adsorption capacity (interrupted line) during dyeing for different initial concentrations.

In a study by other researchers, the main aim of the paper was to compare the dyes differently pre-treated (alkali, acid and enzymes) and dyed (conventional and ultrasonic dyeing) of flax fibers, to determine the effect of different parameters on the sorption and dyeing kinetics. During conventional dyeing, the dyeing rate increased slightly during the first stage of the procedure (first 30 min). Partial desorption was observed after 36 min. By raising the dyeing temperature to 98 °C (after 50 min), the exhaustion increased rapidly, especially for samples pretreated by enzymes and acid, implying a shorter time to reach equilibrium. The amount of dye exhaustion by ultrasound was

higher (95%) and the time to achieve equilibrium was shorter [3].

For the quantitative description of the sorption process, mathematical models of empirical or theoretical nature or sorption isotherms can be applied. Generally, sorption isotherms represent the dependence of the amount of the bound adsorbate per unit mass of adsorbent (q_e) and the equilibrium concentration of a given adsorbate in the observed medium (C_e), at constant temperature, $q_e = f(C_e)$. This dependency is relevant only if the condition of adsorption equilibrium is established in the system and if all other physical and chemical parameters of the medium, in which the process of adsorption is performed, are constant [15].

Diagram in Figure 5 represents interpretation of Langmuir adsorption isotherm for dyeing of a linen cloth at 95 °C, showing the dependency of the parameter ($1/q_e$) in relation to the reciprocal value of the equilibrium concentration of the dye ($1/C_e$).

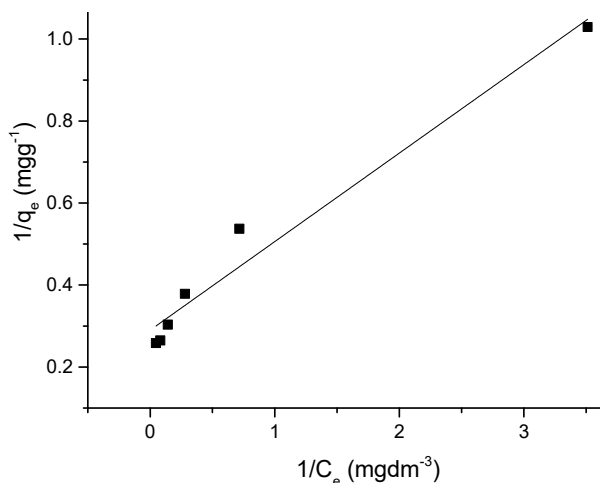


Figure 5. Langmuir linear regression model for equilibrium dyeing of linen fabric.

From the slope and the section of the functional line (curve), the values of the Langmuir constants were determined, $q_m = 3.45 \text{ mg g}^{-1}$ and $b = 1.34 \text{ dm}^3 \text{ mg}^{-1}$, shown in Table 1. They refer to the maximum amount of adsorbate that can bind to the adsorbent and the free energy of adsorption, respectively. The coefficient of determination $R^2 = 0.969$, as a relative measure of the representativeness of the regression line or a measure of the utility of the model, predicts good correlation of the experimental data with the Langmuir model.

If it is assumed that dye adsorption occurs via a Langmuir-type mechanism, adsorption is mainly due to the saturated monolayer adsorption of direct dye molecules onto the flax fiber surface, the adsorption energy is constant and there is no transmigration of the dye molecules in the plane of the fiber surface. It is unlikely that the addition of inorganic electrolyte will

not affect the existence of solely monolayer and that the energy adsorption will remain unchanged; in other words, the acceptability of the Langmuir model was violated and is less likely in this case [15].

Confirmation of this is found in the determination of Langmuir dimensionless constants, equilibrium parameter R_L . The R_L value predicts whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), suitable ($0 < R_L < 1$), or irreversible ($R_L = 0$). From the values for b and the highest initial concentration of red (60 mg dm^{-3}), R_L is determined, with the value of 0.012. Since the value of R_L is very small, very close to zero, this isotherm model should be taken with caution regarding the isotherm which tends to irreversibility in this case.

The diagram of Figure 6 represents the Freundlich isotherm for adsorption of the direct dye onto the adsorbent (linen fabric), for a constant amount of adsorbent and a temperature of 95 °C.

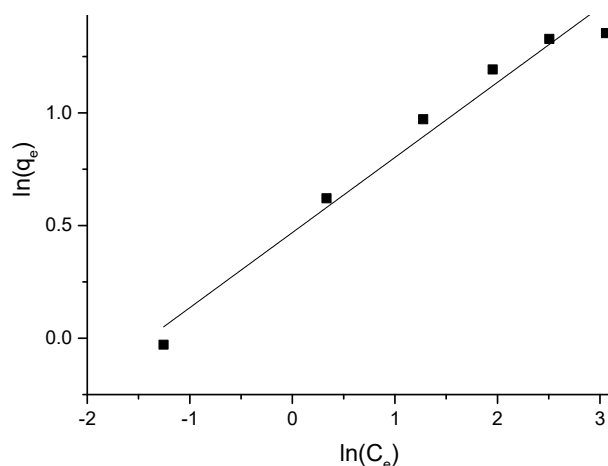


Figure 6. Freundlich linear regression model for equilibrium dyeing of linen fabric.

The Freundlich isotherm implies the existence of a heterogeneous surface with the uneven distribution of the adsorption heat on the surface and with the possibility of formation of multilayer adsorption [16].

Table 1. Analytical equations of linear isotherms with coefficients for the system dye-flax fibers

Models	Analytical model equations	Model parameters	R^2
Langmuir	$\frac{1}{q_e} = \frac{1}{3.45} + \frac{1}{4.62 C_e}$	$q_m \text{ (mg g}^{-1}\text{)}$ $b \text{ (dm}^3 \text{ mg}^{-1}\text{)}$	3.45 1.34 0.969
Freundlich	$\ln q_e = 0.47 + 0.33 \ln C_e$	$K_F \text{ (mg} \cdot \text{g}^{-1} \text{ (dm}^3 \text{ mg}^{-1}\text{)}^{(1/n)})}$ n_F	1.60 3.00 0.973
Temkin	$q_e = 1.79 + 0.72 \ln C_e$	B_T $K_T \text{ (dm}^3 \text{ mg}^{-1}\text{)}$	0.72 11.96 0.985
Flory-Huggins	$\ln\left(\frac{\theta}{C_0}\right) = -5.40 - 0.87 \ln(1-\theta)$	$K_{FH} \text{ (dm}^3 \text{ mg}^{-1}\text{)}$ n_{FH}	0.0045 -0.87 0.999

On the basis of this diagram, the values of Freundlich constants are determined, and *via* them, the competence of this model for describing the process of applied dye adsorption for linen fabric is evaluated. K_F , one of the Freundlich constants, is used as a relative measure of adsorption capacity. A higher value ($K_F = 1.6$ in this case) indicates a higher adsorption capacity.

The other Freundlich constant, n , is an empirical parameter that is changed with a degree of heterogeneity, indicating the degree of non-linearity between the capacity of receiving the dye and concentration of non-adsorbed dye, and relates to the distribution of bound ions to the surface of the adsorbent-fabric. In general, $1/n < 1$ shows that adsorbate is adsorbed enough on the adsorbent, adsorption capacity increases, and there are new positions for adsorption; the higher the value of n , the greater the intensity of adsorption. The results confirm that $n > 1$, *i.e.*, $3 > 1$, or $1/n < 1$, *i.e.*, $1/3 < 1$, that is $0.33 < 1$.

The coefficient of determination for this isotherm is 0.973, which means that the Freundlich model has a slight advantage compared to the Langmuir model.

If it is assumed that dyeing occurs by a mechanism that provides for the Freundlich model, in an early stage of adsorption, the monolayer of adsorbed dye molecules is formed. The formation of multilayers of adsorbed dye molecules at non-specific sites on the fiber immediately follows through the self-association of adsorbed dye molecules. Newly adsorbed dye molecules can associate with previously adsorbed molecules within the substrate. There are also aggregated dye molecules from the bath that can also be adsorbed [16]. Aggregation of the dye within the fiber and, thus, the formation of multi-layers of adsorbed dye molecules is likely to happen, regarding the fact that long and flat molecules of direct dye tend to self-associate in the solution *via* π - π interactions between adjacent dye molecules. Of course, the sorption mechanism by Freundlich predicts the fact that dye aggregation is probably an intrinsic characteristic of the dye-fiber interaction that the inorganic electrolyte can further accelerate.

Adsorption data, analyzed according to a linear form of the Temkin isotherm, are shown in the chart in Figure 7. The results confirm that the Temkin isotherm fitted adsorption data well on the substrate surface for the direct dye. The value of the Temkin constant B_T , related to the heat of dye adsorption on the fiber, is 0.72, whereas the constant K_T has a value of 11.96. The coefficient of determination, R^2 , obtained from the Temkin model (0.985) has a higher value in relation to the previous two isotherms, which offers

advantages in the applicability of the Temkin model to describe the adsorption of direct dyes to the surface of flax fibers.

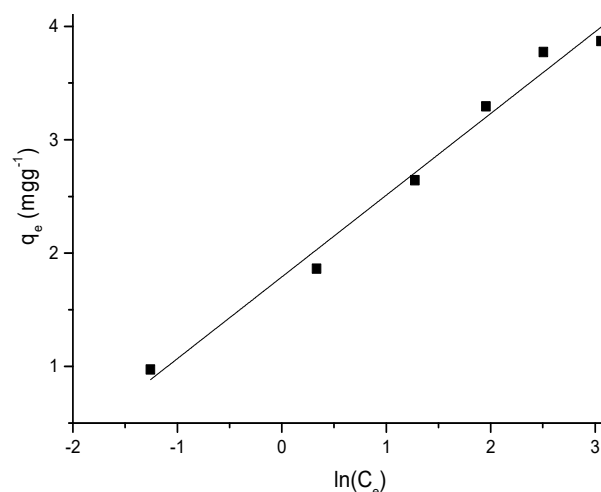


Figure 7. Temkin linear regression model for equilibrium dyeing of linen fabric.

Heat of adsorption, b_T , obtained from the Temkin model, has a value of 4.24 kJ mol^{-1} . With respect to $b_T = -\Delta H$, there is a change of enthalpy $-4.24 \text{ kJ mol}^{-1}$, which implies another exothermic process during dyeing. This adsorption energy will be the sum of all individual adsorptions occurring at different sites-locations on the surface of the adsorbent. In addition to the structure of the dye and substrate, the value of adsorption heat, *i.e.*, change in enthalpy, are highly influenced by the presence of inorganic electrolytes, which directly affects the ability of the interaction and binding, by physical or chemical bonds [11]. Due to small adsorption heat and negative change of the enthalpy ΔH , the interaction of dye and flax fiber is mainly accompanied by reversible physical adsorption supported by weak electrostatic forces (dipolar bonds, van der Waals forces or hydrogen bonds).

Figure 8 gives a diagram of the Flory-Huggins equilibrium adsorption model, which in this case was used to determine the degree of direct dye coverage characteristics of a flax fiber surface.

According to the values of the Flory-Huggins isotherm parameters as well as the values of the coefficient of determination, $R^2 = 0.999$, it can be concluded that this model is ideal for describing direct dye sorption on flax fibers. A positive value of K_{FH} (0.0045) is an indication of the feasibility and spontaneous adsorption.

The obtained value ΔG ($-25.71 \text{ kJ mol}^{-1}$, $95 \text{ }^\circ\text{C}$) is negative, and it decreases with increasing temperature, which indicates that the process of adsorption

in this particular case is favorable, spontaneous in nature and more efficient at higher temperatures. Generally, the change in free energy for physisorption is between -20 and 0 kJ mol^{-1} , while for chemisorption it is in the range of -80 to -400 kJ mol^{-1} [17].

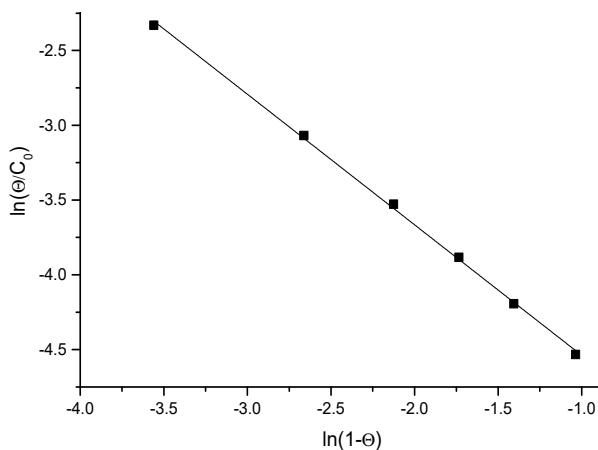


Figure 8. Flory-Huggins linear regression model for equilibrium dyeing of linen fabric.

Decrease in ΔG with increasing temperature (for 95, 60 and 20 °C, ΔG is -25.71 , -22.91 and -20.06 kJ mol^{-1} , respectively) favors the process of direct dye exhaustion to flax fiber from the bath at high temperature. Similarly, as in the interpretation of the Temkin isotherm, the physical adsorption during dyeing of flax fibers with direct dye is confirmed.

Since the degree of area coverage associated with the sticking probability (S^*) of an adsorbate on the adsorbent, the values of the parameter S^* for the adsorption of the direct dye on flax fibers are found. The results show that the values of this parameter increase with increasing dye concentration during dyeing and are all smaller than 1 (minimum value $S^* = 2.43 \times 10^{-7}$ for dye concentration of 10 mg dm^{-3} and maximum value $S^* = 0.0109$ for dye concentration of 60 mg dm^{-3}). This means that there is a favorable bonding of the dye to the fiber or an ability of the adsorbate to remain on the adsorbent indefinitely, which means that there are, in part, elements of chemical adsorption of the dye on the adsorbent.

In addition to the parameter S^* , a value of the energy of activation parameter (E_a) is calculated, which in the process of dyeing at 95 °C and dye concentration of 10 mg dm^{-3} is $35.89 \text{ kJ mol}^{-1}$. The value of activation energy decreased with the increase of dye concentration, and for the highest concentration of 60 mg dm^{-3} was $10.39 \text{ kJ mol}^{-1}$. It is known that the energy of activation for physical adsorption is $5\text{--}40 \text{ kJ mol}^{-1}$, while the chemical adsorption is $40\text{--}800 \text{ kJ mol}^{-1}$ [18]. Thus, this parameter (E_a), the value of which

ranged from 10.39 to $35.89 \text{ kJ mol}^{-1}$, confirmed the fact that the physical sorption is the main mechanism in flax dyeing with direct dye but the existence of chemical contacts (bonds) is not excluded.

Table 1 shows the analytical equations of the linear adsorption isotherms, the values of the adsorption parameters, and the values of the coefficients of determination R^2 . Based on the results from this table, it is confirmed that the Flory-Huggins model dominates, according to coverage of experimental points, $R^2 \approx 1$, although other linear models do not lag behind much. Of all the linear models used, the Langmuir model proved to be the weakest in this case.

CONCLUSION

On the basis of the experimental results, it can be concluded that:

- Dyeing of a linen fabric with direct dye in the presence of inorganic electrolyte in the laboratory conditions gives good results at a temperature of 95 °C with a high degree of exhaustion.
- Increasing the dye concentration during dyeing decreases the degree of exhaustion, while the longer dyeing time gives a greater degree of dye exhaustion.
- A larger amount of dye or a longer dyeing period yields a greater amount of adsorbed dye per unit mass of fabric.
- All four models can be used to describe the direct dye adsorption on flax fibers; however, the Flory-Huggins model is preferred because of the maximum value of determination coefficient R^2 .

With regard to the mechanism of adsorption of direct dye on flax fiber, it can be said that due to the extremely complex nature of the dye-dye, dye-electrolyte or dye-fiber interactions, it was difficult to accurately define real events, but it is indisputable that, based on the analysis of the results of multiple adsorption models, physical adsorption dominates where secondary types of chemical bonds are favored, dipolar, van der Waals, hydrogen, etc.

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NAUČNI RAD

STUDIJA SORPCIJE DIREKTNE BOJE NA LANENA VLAKNA TOKOM BOJENJA

Članak predstavlja studiju sorpcije direktne boje na laneno vlakno tokom procesa bojenja u prisustvu neorganskog elektrolita. Prethodno pripremljena lanena tkanina je podvrgnuta bojenju standardnim postupkom uz variranje koncentracije i vremena bojenja. Rezultati su zadovoljavajući s obzirom na to da otkrivaju karakter sorpcije direktne boje za vlakno kao i kapacitet i energiju adsorpcije, na osnovu čega se može optimizovati proces bojenja. Porast koncentracije boje u rastvoru pri bojenju opada, duže vreme bojenja povećava stepen iscrpljenja. Adsorbovane količine adsorbata na adsorbentu raste tokom povećanja početne koncentracije i vremena bojenja. Modeli Langmuir, Freundlich, Temkin i Flory-Huggins mogu se upotrebiti za opis adsorpcije direktne boje na laneno vlakno, s tim da se prednost daje modelu Flory-Huggins-a zbog njegovih osobenosti u opisu sorpcije kao i maksimalne vrednosti koeficijenta determinacije.

Ključne reči: bojenje, lan, Freundlich, Flory-Huggins, Langmuir, Temkin.